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Quantum treatment of the Anderson-Hasegawa model – superexchange and polaronic heat capacity

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Abstract : We revisit the Auderson-Hasegawa double-exchange model and critically examine its exact solution when the core spins are treated quantum mechanically. We show that the quantum effects, in the presence of an additional superexchange interaction between the core spins, yield a term, the significance of which has been hitherto ignored. The quantum considerations further lead to new results when polaronic effects, believed to be ubiquitous in manganites due to electron-phonon coupling, are included. The consequence of these results for the magnetic phase diagrams and the thermal heat capacity are analysed

Keywords : Double-exchange, superexchange, electron-phonon interaction

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1. Introduction

The discovery of colossal magnetoresistance (CMR) [1] in rare-earth manganites, with the general composition $R_{1-x}A_xMnO_3$ (where R and A are rare-earth and alkaline earth ions, respectively), have renewed intense investigations in these materials. Zener [2] first proposed the 'Double Exchange' (DE) model for appropriate interpretation of ferromagnetism and metallicity in the doping range $0.2 < x < 0.4$. The basic unit which is the illustrative of manganese perovskites is the Mn^{3+}-O-Mn^{4+} triad. This can be encapsulated within a simple two site model of Andersen and Hasegawa [3–5]. One of the directions in which the Anderson-Hasegawa treatment has been extended is to recognize the importance of an additional superexchange term between the core spins proportional to $S_1.S_2$. It has been assumed in the literature till now that the shperexchange term can be simply taken as an extra term to be added to the Hamiltonian and that the large Hund's rule coupling affects only the process of charge transfer in these systems. For simplicity, usually the core spins are considered classical though the t_{2g} spins of Mn^{3+} and Mn^{4+} are only 3/2. The exact quantum treatment [6] of the core spins to calculate the double exchange Hamiltonian as well as superexchange interaction between adjacent localized core spins, in the limit of strong Hund's rule coupling, shows that the classical approximation is not a proper generalization of the system.

As the value of the core spins in most studied CMR systems is indeed finite – three-halves for manganese – it is important to delineate the quantum *versus* classical effects, especially while considering additional phenomena, *e.g.*, polaron-induced hopping and thermodynamics. With this aim in mind, we organize the paper as follows. We present in Section 2, the issue of polaron-assisted hopping in the light of our fully quantum calculation. The results in this section are then employed in Section 3 for the computation of heat capacity and phase diagram, wherein we also specify the difference between our results and those which treat the core spins classically [7]. Finally, in Section 4, we present some concluding remarks.

2. Formulations

Our starting point is the Hamiltonian for a two site one electron model, including the superexchange interaction, given by

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$$H_{DE} = -t\sum(c_{1\tau}^{\dagger}c_{2\tau} + h.c.) - J_H\sum_{i=1}^{2} S_i\sigma_i + JS_1.S_2 . \quad (1)$$

Here, t is the hopping matrix element for the itinerant electron between the two sites, $c_{1\tau}^{\dagger}$ ($c_{i\tau}$) is the creation (annihilation) operator of the itinerant electron at site i having spin projection τ, J_H is the Hund's rule coupling strength, S_i is the core spin at site i and σ_i is the spin of the itinerant electron at the site i. The parameter J is the superexchange interaction strength between the core spins in the nearest neighbour sites. For our case, we consider $|S_i| = S$, *i.e.* the core spins on all the sites are taken to have the same value.

From the exact eigenvalue of H_{DE}, we may take the large J_H limit by expanding upto $O(1/J_H)$ and write an effective Hamiltonian for the two-site one electron case as [6]

$$H_{\text{eff}} = -t\frac{\left(S_0+\frac{1}{2}\right)}{2S+1}\left(c_1^{\dagger}c_2 + h.c.\right) + JS_1.S_2$$

$$+\Delta E_J(\hat{n}_1 + \hat{n}_2) . \quad (2)$$

Here, S_0 is the magnitude of the total spin (localized plus itinerant) given by $|S_1 + S_2 + \sigma|$, and

$$\Delta E_J = \frac{J}{2}\frac{2S-\bar{S}'}{2S+1}(\bar{S}'+1), \quad (3)$$

where $S' = S_0 - 1/2$. The spin index τ has been omitted from eq. (2), for the sake of brevity, as the spin moment of the itinerant electron in any case is parallel. The first term in eq. (2) is the one obtained by Anderson-Hasegawa when the localized spin is treated quantum mechanically. The third term, represented by the number operators $n_{1(2)}$ for the itinerant electron, modifies the double-exchange mechanism in the presence of the superexchange interaction given by the second term in eq. (2). This on-site term, proportional to ΔE_J, we should emphasize, is hitherto not widely considered in the literature, and is a direct consequence of the quantum nature of the localized spin. It is to be noted that in the ferromagnetic limit (*i.e.*, $\bar{S}' = 2S$) this term vanishes exactly. In the classical limit, this extra term goes to zero [6] in both the ferromagnetic as well as the antiferromagnetic limits. Thus, we see a clear distinction between the classical and the quantum results in the antiferromagnetic limit. We emphasise that in taking the purely classical expression, one actually loses the effect of the quantum fluctuations which are present in these systems not only because of the fluctuating spins but also due to the hopping being correlated with the spins on the lattice. A variety of interesting physical phenomena could be studied by taking into consideration the quantum Hamiltonian One of these concerns the polaron effects, which are discussed below.

Experiments in manganites – both thermodynamic and transport – seem to suggest the importance of polaron formation and the consequent localization of charge carriers [8]. The minimal model which reflects such lattice carrier interaction on the double-exchange can be introduced by incorporating the Holstein mechanism on the Anderson-Hasegawa Hamiltonian. In the limit of large Hund's rule coupling, we may write a two-site Anderson-Hasegawa-Holstein Hamiltonian as,

$$H = H_{\text{eff}} + g_1\omega_0\sum_{i=1}^{2} n_i(b_i + b_i^{\dagger}) + g_2\omega_0\left[n_1(b_2 + b_2^{\dagger})\right.$$

$$\left. + n_2(b_1 + b_1^{\dagger})\right] + \omega_0\sum_{i=1}^{2} b_i^{\dagger}b_i \quad (4)$$

where, $g_1(g_2)$ denotes the on-site (intersite) electron-phonon coupling strength. Note that we have considered a single phonon mode for interatomic vibrations of frequency ω_0 for which b_i and $b_i^{\dagger}$ are the annihilation and creation operators.

We separate out the in-phase mode and the out-of-phase mode by introducing new phonon operators $a = (b_1 + b_2)/\sqrt{2}$ and $d = (b_1 - b_2)/\sqrt{2}$ in the Hamiltonian. The in-phase mode does not couple to the electronic degrees of freedom whereas the out-of-phase mode does, leading to a Hamiltonian H_d, given by,

$$H_d = \omega_0 d^{\dagger}d + \Delta E_J\sum_{i=1}^{2} n_i - t\left(\frac{S_0+\frac{1}{2}}{2S+1}\right)(c_1^{\dagger}c_2 + H.c.)$$

$$+ g_-\omega_0(n_1 - n_2)(d + d^{\dagger}) + JS_1.S_2 , \quad (5)$$

which represents an effective electron-phonon system. Following [9], we use a Modified Lang-Firsov (MLF) transformation with variable phonon basis and obtain,

$$\tilde{H}_d = e^R H_d e^{-R}$$

$$= \omega_0 d^\dagger d + \sum_i \epsilon_p n_i - t\frac{S_0+\frac{1}{2}}{2S+1}\left[c_1^\dagger c_2 \exp(2\lambda(d^\dagger - d))\right.$$

$$\left. + c_2^\dagger c_1 \exp(-2\lambda(d^\dagger - d))\right] + JS_1.S_2 + \Delta E_J$$

$$+ \omega_0(g_- - \lambda)(n_1 - n_2)(d + d^\dagger), \qquad (6)$$

where $R = \lambda(n_1 - n_2)(d^\dagger - d)$, λ is a variational parameter related to the displacement of the d oscillator, $g_- = (g_1 - g_2)/\sqrt{2}$ and $\epsilon_p = \Delta E_J - \omega_0(2g_- - \lambda)\lambda$. The basis set is given by $|\pm,N\rangle = \frac{1}{\sqrt{2}}(c_1^\dagger \pm c_2^\dagger)|0\rangle_e|N\rangle$, where $|+\rangle$ and $|-\rangle$ are the bonding and the antibonding electronic states and $|N\rangle$ denotes the N-th excited oscillator state within the MLF phonon basis. The diagonal part of the Hamiltonian $\tilde{H}_d$ in the chosen basis is treated as the unperturbed Hamiltonian (H_0) and the remaining part of the Hamiltonian $H_1 = \tilde{H}_d - H_0$, as the perturbation. The unperturbed energy of the state $|\pm,N\rangle$ is given by

$$E^{(0)}_{\pm,N} = \langle N,\pm|H_0|\pm,N\rangle$$

$$= N\omega_0 + \epsilon_p \mp t_{eff} \sum_{i=0}^{N} \frac{(2\lambda)^{2i}}{i!}(-1)^i N_{C_i}$$

$$. + JS_1.S_2, \qquad (7)$$

where $t_{\text{eff}} = t\frac{S_0+\frac{1}{2}}{2S+1}\exp(-2\lambda^2), N_{C_i} = \frac{N!}{(N-i)!i!}$ The general off-diagnoal matrix elements of H_1 between the two states $|\pm,N\rangle$ and $|\pm,M\rangle$ may be calculated for $(N - M) > 0$ as in Ref. [9]. The unperturbed ground state is the $|+\rangle|0\rangle$ state and the unperturbed energy, $E_0^{(0)} = \epsilon_p - t_{\text{eff}} + JS_1.S_2$. However, in this exact quantum limit of core spins, for given values of g_- and J, $E_0^{(0)}$ can have four values corresponding to ferromagnetic (FM), canted 1 (CA1), canted 2 (CA2) and antiferromagnetic (AFM) orientation of the two spins for $|S_{12}| = |S_1 + S_2| = 3, 2, 1, 0$ respectively. Minimizing the unperturbed ground state energy λ is calculated and is given by

$$\lambda = \frac{\omega_0 g_-}{\omega_0 + 2t_{\text{eff}}} \qquad (8)$$

We have evaluated the perturbation correction to the energy upto the sixth order and the wave function upto the fifth order. The convergence of the perturbation series is very good for $t/\omega_0 \leq 1$. To obtain the ground state spin order of the core spins we calculate the energy for each set of values of g_- and J with four possible S_{12} and find out the combination for which the energy is the minimum.

It is expected that the charge transfer from site '1' to '2' depends on the spin order of the core spins as well as the electron-phonon interaction. In the double-exchange model, the effective hopping reaches its maximum value in the ferromagnetic state and decreases as it approaches the antiferromagnetic limit. Moreover, in a lattice, the electron produces lattice deformations and which in turn localize the electron for strong electron-phonon coupling. To study the polaronic character one calculates the static correlation functions $\langle n_1 u_1\rangle_0$ and $\langle n_1 u_2\rangle_0$ where u_1 and u_2 are the lattice deformations at sites 1 and 2 respectively, produced by an electron at site 1 [9,7]. In the present report with a two-site one electron model, following [7], we calculate $-\langle n_1(u_1 - u_2)\rangle_0 / g_- = \frac{\lambda^{\text{corr}}}{g_-}$ and study the nature of the polaron crossover for different ranges of g_- and J. In the 'large' polaron limit this parameter takes a small value, while with increasing electron-phonon coupling it tends to unity, showing a distinct crossover from 'large' to 'small' polaron behavior. The measure of delocalization of the electron for various ranges of g_- as well as J will be evident from the kinetic energy. So we have also calculated the kinetic energy, given by,

$$t_{\text{eff}}^{KE} = -E_{Kin} = \langle \psi_G \left| \frac{S_0+\frac{1}{2}}{2S+1}\right.\left[c_1^\dagger c_2 \exp(2\lambda(d^\dagger - d))\right.$$

$$\left. + c_2^\dagger c_1 \exp(-2\lambda(d^\dagger - d))\right]\Big|\psi_G \qquad (9)$$

where ψ_G is the ground state wave-function, is evaluated upto the fifth order in the perturbation. The numerical evaluation of E_{Kin} will be presented below in Section 3.

3. Phase diagrams and specific heat

If the localized core spin at each site is 3/2 then the possible values of $|S_1 + S_2| = S_{12}$ are 3, 2, 1 and 0. The

ferromagnetic (FM) and antiferromagnetic (AFM) orders are obviously related to $S_{12} = 3$ and 0, whereas $S_{12} = 2$ and 1 are referred as canted 1 (CAl) and canted 2 (CA2) states respectively. The Figure 1 shows the phase diagram

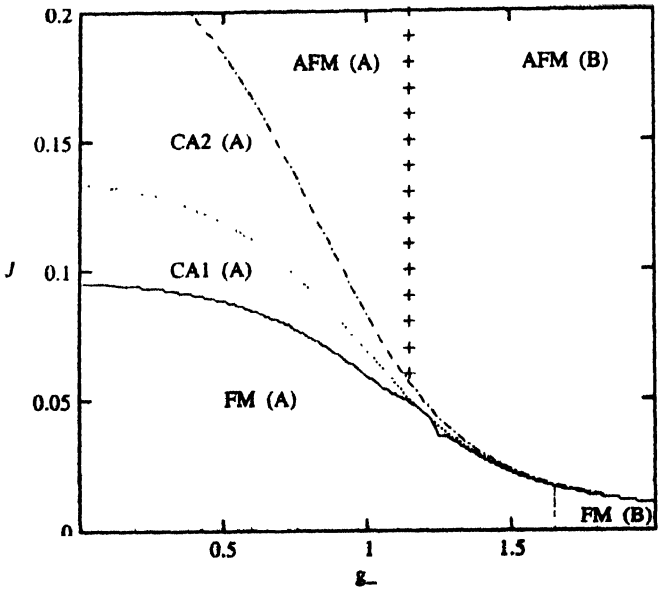

Figure 1. The g_- *vs* J phase diagram for $S = 3/2$, $t = 1$ and $\omega_0 = 1$. (A) and (B) denote large polaron and small polaron regions, respectively.

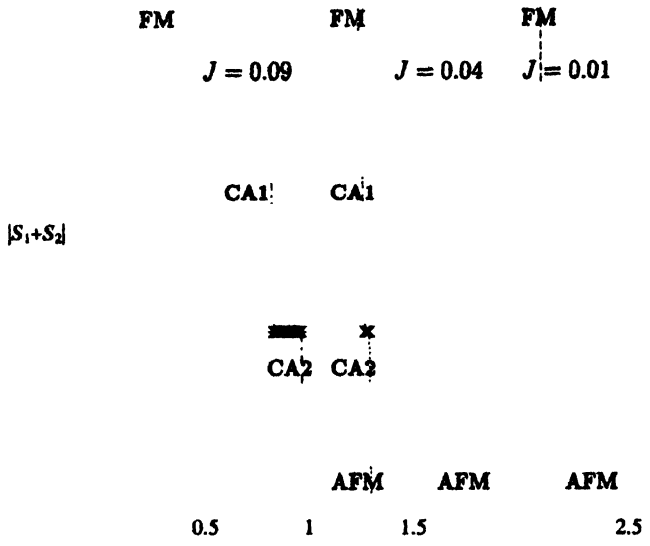

Figure 2. Variations of ground state spin configuration $|S_1 + S_2|$ with g_- for $t = 1$ and $J = 0.01$, 0.04 and 0.09 (in units of $\omega_0 = 1$).

for the four possible spin orders for our system, in the g_- *vs* J plane. For small values of g_- and J, the FM state is the most stable one, and with increasing J, the ground state first becomes CAl and then CA2. For a very large value of the superexchange interaction J, the system is in an AFM order for any value of g_-. However, with increasing electron-phonon interaction g_- the CAl and CA2 phase become narrower. Indeed, for larger values of g_- the FM state appears for very low J but with a small increase of J the system transists to the AFM phase. The CAl and CA2 phases in fact do not appear at all as the phase changes from the FM to AFM state with increasing superexchange interaction J, for large values of g_-. It can be further shown that for a very large value of g_- the ground state is AFM for any value of J. Recently Capone and Ciuchi [10] also got similar phase diagram.

It is evident from the phase diagram that for a particular value of J the ground state changes as the electron-phonon coupling (g_-) increases (Figure 1). But the change of phase from one to another is not continuous with g_- for the quantum consideration of the core spins. This is shown in Figure 2. For small values of $J = 0.01$, the FM state exists even for a large value of g_- and then it sharply changes to the AFM state. On the other hand, for larger values of $J = 0.04$, 0.09, the system passes sharply to the canted phases (CA1 and CA2) and then the AFM state, with increasing g_-. For $J = 0.04$ the CA1 and CA2 regimes are very narrow and for $J = 0.09$ the CA1 and CA2 orders persist for a wider range of g_-. This is to be contrasted with the classical core spin model in which a similar study [7] shows that the transitions to different core spin orientations are continuous for the same range of values for g_- and J. In the classical case only three phases (FM, AFM and Canted) are present. The relative angle θ between classical core spins can take any value from 0 to π, so any spin orientation other than FM ($\theta = 0$) and AFM ($\theta = \pi$) yields a canted phase. Hence, in the classical limit of the core spins, for certain values of J, the FM-AFM transition is a smooth and continuous transition with g_-, whereas for spin 3/2, the FM-AFM transition with g_- is never continuous for any J.

The probability of hopping of the itinerant electron from site to site is a maximum in the FM state as would be expected from the double-exchange mechanism. But, for a very strong electron-phonon coupling g_-, the electron may be localized forming a small polaron. For low values of J we find both small and large polaron ground states in the FM phase (Figure 3). The large to small polaron crossover is indicated by the relative deformation of the two lattice sites which is measured by the static correlation function $\frac{\lambda_{corr}}{g_-}$. In Figure 3 the kinetic energy t_{eff}^{KE} is large for small values of g_- where the polaron

large, and for large $g_{\_}$ the kinetic energy reduces rapidly, while $\frac{\lambda_{corr}}{g_{\_}}$ rises, showing a smooth crossover to the small polaron regime. The classical and quantum formulations of the double-exchange model turn out to be the same in the FM limit of the core spins. So the nature of the kinetic energy and the polaron crossover in the FM state, as shown in Figure 3, will be unaltered in the classical limit of core spins. However, in the AFM limit the two approaches (classical and quantum) are not equivalent, as has been argued earlier also. In the $S \rightarrow \infty$ limit the hopping probability is zero for the AFM case, while for $S = 3/2$ the parameter modifying the hopping probability t, takes a finite value 0.25 resulting in a finite charge transfer, even in the AFM limit.

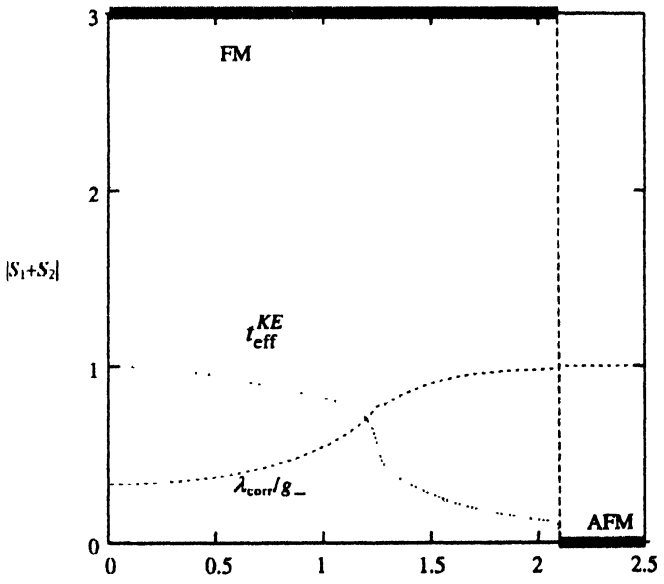

Figure 3. Variations of t_{eff}^{KE} and $\lambda_{corr}/g_{\_}$ with $g_{\_}$ for $t = 1.0$, $J = 0.01$.

In Figure 4, we show the nature of variation of the kinetic energy as well as the polaron crossover in different magnetic ground states. For $J = 0.09$ the ground state is FM for low $g_{\_}$ and with increasing $g_{\_}$ the ground state changes sharply to CA1, CA2 and lastly to the AFM state. Since at each transition (from FM → CA1 → CA2 → AFM) the effective hopping reduces due to the double-exchange interaction, it is obvious that the kinetic energy will show a sharp drop at each transition point. It is expected that the polaron crossover will also show concomitant sharp jumps at each magnetic transition and the crossover to small polaron behaviour will occur at lower value of $g_{\_}$ than in the FM limit. This is shown clearly in Figure 4. It is further evident that in a double-exchange system, both the magnetic transitions and the electron-phonon coupling localize the electron, when the polaron crossover and magnetic transitions are overlapping. The locations of the large polaron region (A) and the small polaron region (B) are indicated in the $g_{\_}$ *vs* J phase diagram (Figure 1). Thus the results presented in Figure 3 and Figure 4, have a bearing on the transport behaviour of our model.

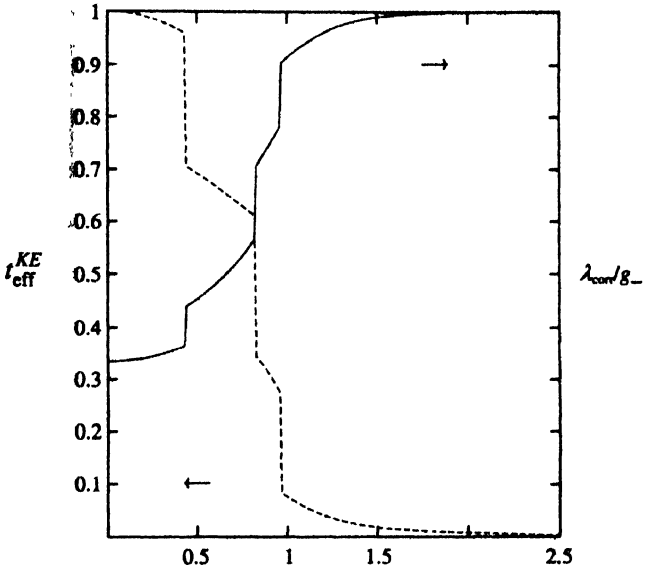

Figure 4. Variations of effective kinetic energy t_{eff}^{KE} (dashed line) and polaron crossover $\lambda_{corr}/g_{\_}$ (solid line) with $g_{\_}$ for $t = 1.0$, $J = 0.09$. The sharp jumps in t_{eff}^{KE} and $\lambda_{corr}/g_{\_}$ occur at values of $g_{\_}$ where the magnetic transitions take place (see Figure 2).

Having discussed transport we now redirect our attention to thermodynamic properties. According to experiments [11], the specific heat C_v of CMR manganites has contributions from conduction electrons, lattice and spin waves. Very recently we have computed [12] the heat capacity using an exact treatment of the Anderson-Hasegawa two site model incorporating the presence of superexchange and polarons. Our calculated results point to the dominance of lattice contribution in the ferromagnetic region. In Figure 3(a) of Ref. [12], we have shown that in the FM ground state the T^3 behaviour of the specific heat is more pronounced which is in qualitative agreement with experimental findings [11]. However, while calculating the heat capacity in $S \rightarrow \infty$ (classical core spin) limit it is seen that spin wave contribution will be dominant *i.e.*, $C_v \propto T^{3/2}$ in FM case. This is depicted in Figure 5. Dominance of the $T^{3/2}$ behaviour of specific heat in classical limit is due to

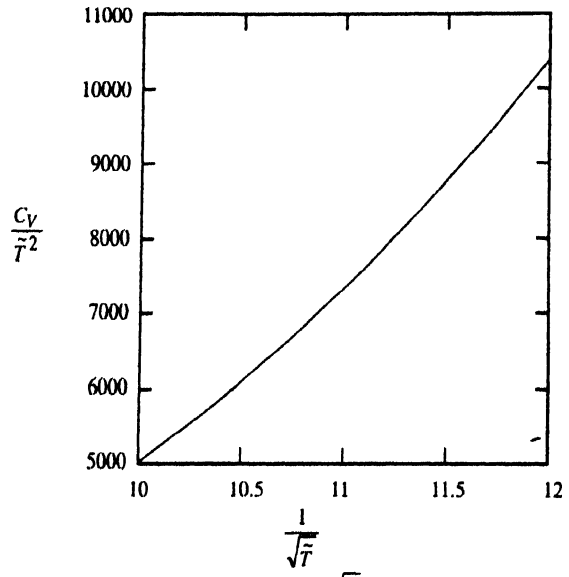

Figure 5. Variaition of $Cv/\tilde{T}^2$ with $1/\sqrt{\tilde{T}}$ for $g_- = 0.1$, $J = 0.02$, $t = 1$ and $\omega_o = 1$. Here Cv is in arbitary units and the effective temperature $\tilde{T} = k_B T\omega_o$. the ground state is *FM* and the local spins are taken classical ($S \to \infty$).

averaging over all possible relative orientations of core spins. The difference in the quantum and classical cases for specific heat, as far as the core spins are concerned, is exemplified in Figure 2 of Ref. [12] for FM case. The quantum results evidently yield the correct low-temperature limit.

4. Conclusions

In the present paper, we discuss the quantum effects in the presence of the superexchange interaction in the Anderson-Hasegawa double exchange model. Including the Holstein interaction term in this quantum double exchange model, we analyse the consequences of classical and quantum limit of core spins, by calculating magnetic phase diagrams, polaron crossover and thermal heat capacity. The discreteness, associated with the effective hopping as a result of quantum nature of the local spin, has significant consequences for magnetic phases and thermodynamic properties.

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